Electrochemical lability of glycine in acid media

Arvydas Survila[*],

Stasė Kanapeckaitė

Center for Physical Sciences and Technology,
Institute of Chemistry,
Saulėtekio Ave. 3,
10222 Vilnius, Lithuania

Electrochemical lability of different glycine species is considered on the basis of voltammetric data obtained for hydrogen evolution on the copper electrode in weakly acidic glycine solutions at different potential sweep rates (v). Voltammograms contain well-defined current peaks the height of which depends on both solution pH and glycine concentration. Current peaks and their potentials vary linearly with $\sqrt{v}$ and log v, respectively, this being typical of the electrochemical processes controlled by diffusion and charge transfer.

To characterise system lability, peak coordinates and convolutive transforms of voltammograms are analysed. The results show that protons attached to different groups in a glycine molecule exhibit different mobility. In contrast to the protonated amino group, the release of a proton from the carboxylic group proceeds significantly faster. Consequently, protonated species $^+H_3N-CH_2-COOH$ can be treated as labile proton donors, whereas zwitterions $^+H_3N-CH_2-COO^-$ do not fall into this category.

Keywords: glycine, lability, hydrogen evolution, LPS voltammetry

INTRODUCTION

Glycine H_2N-CH_2-COOH is the simplest amino acid that is widely distributed in nature as an integral part of many vital substances. Due to the presence of acidic and basic groups, this compound is able to take part in a variety of interactions. Besides, glycine falls into the category of substances which can form coordination compounds with most metal ions. Stable complexes are formed due to a strong bond involving an unshared pair of electrons at the nitrogen atom. Until now, this ligand has been of increasing interest, since it can be industrially applied in plating processes without a negative impact on environment.

Electrodeposition of metals involving complex compounds is usually accompanied by various chemical stages, whose role in the total electrochemical process must be taken into account. Glycine, as a ligand, is not an exception in this respect. It is able to interact not only with metal ions but also with hydronium ions, thus forming various protonated forms. These components determine to a great extent the complexation degree at the electrode surface and, as a consequence, the character of the voltammetric characteristics of the process [1].

To estimate quantitative chemical interactions, their kinetic data are required to determine the lability of the system. In contrast to equilibrium characteristics, such data are met in the literature more rarely. After the well-known polarographic studies carried out by Koutecky and Brdička more than 50 years ago, not much kinetic data has been published. In this regard, mention should be made of a research [2] performed with a sinusoidal hydrodynamic modulated rotating disk electrode. We used some of data obtained in [2] to characterise the electrochemical lability of acetic acid [3, 4].

Undoubtedly, the conclusions concerning the lability of the carboxyl group in acetic acid can not be directly transferred to glycine; therefore, this object requires a separate study. To assess system lability, we used linear potential sweep (LPS) data on hydrogen evolution, assuming that glycine can act as a proton donor in this process. We think that the data obtained could be useful not only for electrochemical kinetics, but also in other fields of science that study chemical transformations of amino acids.

[*] Corresponding author. Email: arvydas.survila@ftmc.lt

EXPERIMENTAL

Solutions were prepared using deionised water, glycine (Aldrich), and $NaClO_4 \cdot H_2O$ (Fluka) as a supporting electrolyte. Specified values of pH were adjusted by addition of $HClO_4$ or NaOH. Solutions were deaerated before experiments with argon stream over 0.5 h.

To prepare the working electrodes, a 1 cm² platinum disc was coated with 5–7 µm thick copper in the solution containing (g dm⁻³): $CuSO_4 \cdot 5\,H_2O$ – 250, H_2SO_4 – 50. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed. More detailed characteristics of surface morphology are given elsewhere [3].

LPS voltammetry was performed using a potentiostat/galvanostat REF 600 from Gamry Instruments. Voltammograms were recorded at a potential sweep rate ranging from 0.01 to 0.2 V s⁻¹. In all cases, cathodic scans were applied, starting with the open-circuit potential.

The electrode potential was measured in reference to the Ag | AgCl | KCl(sat) electrode and was converted to the standard hydrogen scale. All experiments were performed at 20°C.

RESULTS AND DISCUSSION

Simulations of distribution show (Fig. 1) that two glycine species, viz. zwitter ion $^+H_3N–CH_2–COO^-$ and its protonated form $^+H_3N–CH_2–COOH$, dominate in the acid medium. Both particles, designated further as LH and LH_2^+, are capable of splitting off the protons (one and two, respectively), which further convert into hydronium ions. On this basis, the total concentration of proton donors and acceptors (c_H) might be expressed as follows [1]:

$$c_H = [H^+] + [LH] + 2\,[LH_2^+] - [OH^-]. \qquad (1)$$

However, one crucial question should be clarified: is Eq. (1) valid for *labile donors,* and, if it is not, what is the expression in this case? Unfortunately, we failed to find any data concerning the kinetics of formation of protonated glycine species, so we must resort to some analogies. It is known for acetic acid [2] that its dissociation and association rate constants are, respectively, 3.46×10^6 s⁻¹ and 1.28×10^{11} dm³ mol⁻¹ s⁻¹. Our studies have shown [3, 4] that acetic acid behaves under LPS conditions like a labile donor of protons. Although the amino group in glycine has a certain effect on the carboxyl group, it is possible to expect that the dissociation of the –COOH group will also be sufficiently fast. However, it remains to be seen what mobility of proton is at the amino group. In order to obtain an answer to the questions posed, it is necessary to analyse the current–voltage data on the evolution of hydrogen in the glycine system.

Similarly to the acetate system [3, 4], the open-circuit potentials of the Cu electrode in glycine solutions are for
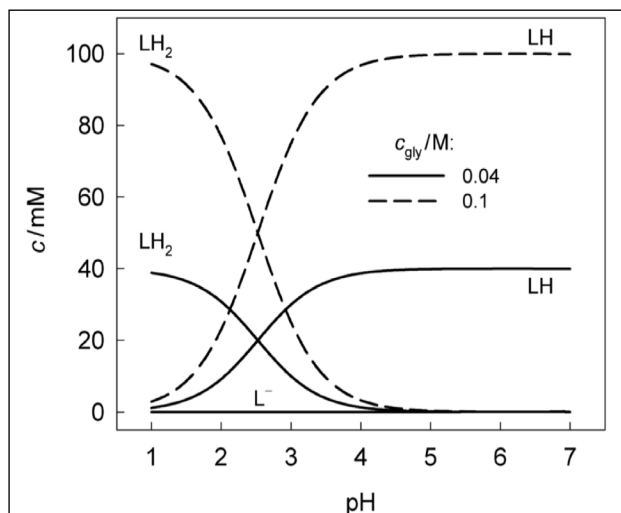

Fig. 1. Distribution of ligand species vs pH in the solutions containing 0.04 M (solid lines) and 1 M (dashed lines) glycine

some hundred mV higher than the equilibrium potentials following from the Nernst equation for the hydrogen electrode. Obviously, copper exhibits such properties due to the absence of dissolved hydrogen in glycine solutions deaerated with argon. Besides, as in the acetate system, long tails in LPS voltammograms with a rather low current density are observed, and an increase in the rate of the cathodic process occurs only at ~ –0.6 V (Figs. 2 and 3). This can be due to very low rate constants (effective exchange currents) of the electrochemical process. Current peaks (i_p) increase with a potential sweep rate v. Besides, their height depends on both solution pH and glycine concentration (Fig. 2), this being indicative that the certain glycine species take part in the hydrogen evolution as proton donors.

The characteristics of peak coordinates are as follows: peak potentials (E_p) vary linearly with log v (inset in Fig. 3); $i_p – \sqrt{v}$ plots are also linear and pass the origin (Fig. 4). Such behaviour is typical of simple redox processes that are controlled by diffusion and charge transfer. This leads to the idea of using the relationships derived for these processes (see, e.g. [5]), with the replacement of the reactant concentration with the total concentration c_H. Such a substitution is reasonable in the case of labile systems [1]. Then

$$i_p = 0.282nF\sqrt{\frac{\pi F}{RT}\alpha v D}\; c_H, \qquad (2)$$

$$E_p = \text{const} - \frac{RT}{2\alpha nF}\ln v. \qquad (3)$$

It follows from the data in Fig. 3 and Eq. (3) at $n = 1$ that the cathodic charge transfer coefficient $\alpha = 0.55$. After setting this value into Eq. (2), two unknown quantities (c_H and the effective diffusion coefficient D) remain.
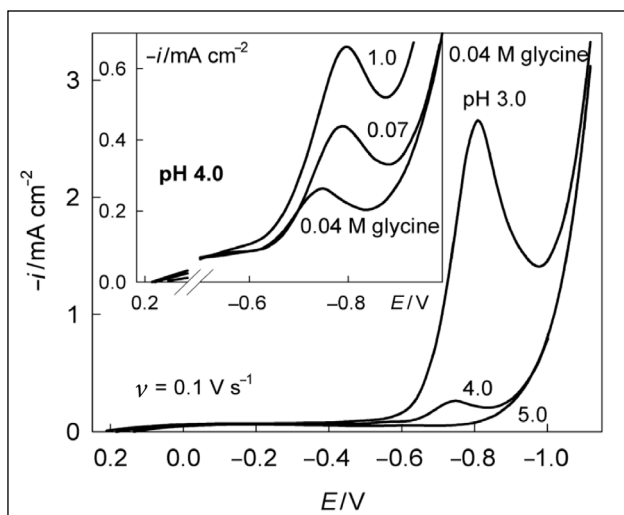
Fig. 2. The effect of pH and glycine concentration (inset) on the LPS voltammograms obtained at $v = 0.1\,V\,s^{-1}$
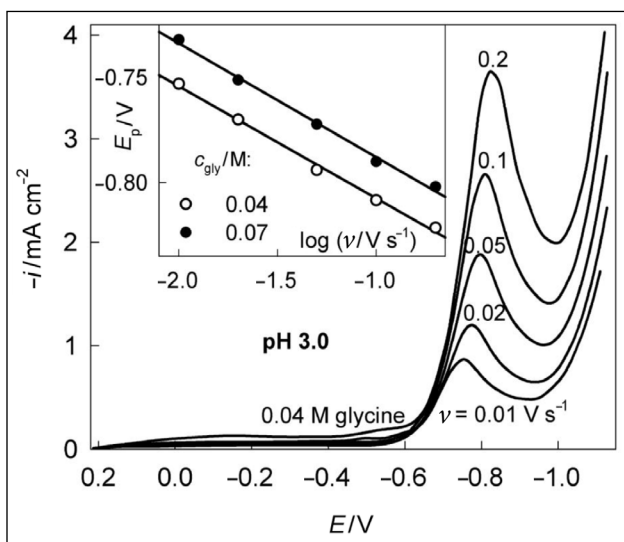

Fig. 3. The effect of the potential sweep rate on the LPS voltammograms obtained for 0.04 M glycine solutions at pH 3. Variations of the peak potential with v are shown in the inset in semilogarithmic coordinates

To exclude the parameter v from Eq. (2), it is convenient to operate with the derivative $\partial i_p / \partial \sqrt{v}$ (see the inset in Fig. 4).

First let us use the data of Fig. 1 to determine the c_H values by Eq. (1), assuming that this relationship is valid for labile proton donors. Then Eq. (2) yields unreal values of $D \sim 10^{-7}\,cm^2\,s^{-1}$, which are significantly lower than the expected quantities. The result obtained shows that certain particles should be excluded from Eq. (1). Assuming that the proton attached to the amino group is not sufficiently mobile, the zwitterion LH should be excluded from consideration and the LH_2 should be treated as the particle containing only one mobile proton, which is split off from the carboxyl group. As a result, we get that
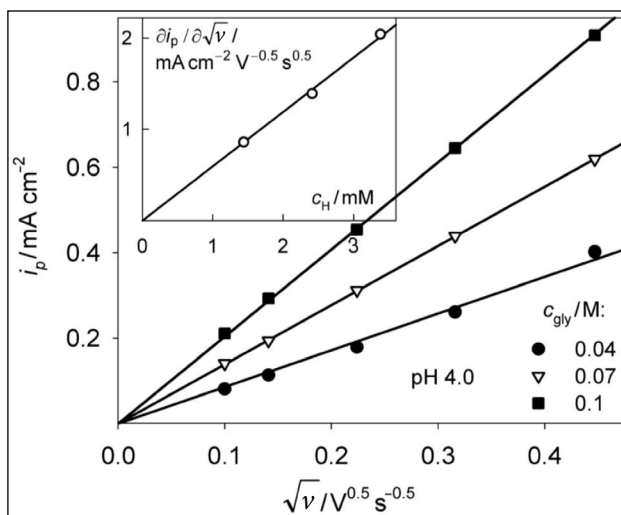

Fig. 4. Variations of peak currents with $\sqrt{v}$ obtained at pH 4 and different glycine concentrations. Slopes of these linear dependences are plotted vs c_H in the inset

$$c_H = [H^+] + [LH_2^+] - [OH^-]. \tag{4}$$

This new modification of Eq. (1) was used in the analysis; some representative results are presented in the inset of Fig. 4. A substantially more acceptable $D = 7 \times 10^{-6}\,cm^2\,s^{-1}$ follows from these data, when Eqs. (2) and (4) are used.

Finally, it is possible to use another way for assessing the lability of the system. It is based on the equation that determines the change in the surface concentration when the current passes:

$$c_H(t) \equiv c_{H,b} - c_{H,s}(t) = -\frac{1}{nF\sqrt{\pi D}} \int_0^t \frac{i(t-u)}{\sqrt{u}} \psi(u)\,du. \tag{5}$$

Here the variable t in the time-dependent current density $i(t)$ is replaced by the auxiliary variable $(t - u)$. Additional subscripts s and b denote the surface and bulk concentrations; the function $\psi(u)$ takes into account the existence of a δ-thick diffusion layer (see [1]). We should like to point out the importance of Eq. (5): since it contains no kinetic characteristics of chemical steps, this relationship is suitable for determining the total surface concentration in both labile and inert systems.

If the system is sufficiently labile, the loss in the surface concentration of the electrically active particles (hydronium ions), caused by the charge transfer process, is easily compensated by fast chemical stages. Then, the concentrations of all particles containing H^+ ions tend to zero at sufficiently high cathodic overvoltages (e.g. in the region of limiting current, where $c_{H,s}(t) \to 0$). If a certain protonated particle is sufficiently inert, it can be eliminated from consideration. Then only the labile components will be taken into account by Eq. (5). The transformation of the experimental data

according to Eq. (5) shows (Fig. 5) that the functions $\Delta c_H(t)$ increase with time moving on the characteristic plateau. Here is a limit of $\Delta c_H(t)$ that approaches the respective bulk concentration $c_{H,b}$ determined by Eq. (4) and indicated by a dotted line in Fig. 5. Such results are obtained at quite acceptable values of D equal to $(8.4 \pm 0.4) \times 10^{-6}$ cm^2 s^{-1}. A somewhat higher $D = 1 \times 10^{-5}$ cm^2 s^{-1} characterises acetic acid molecules [6], which are smaller in size as compared with glycine.
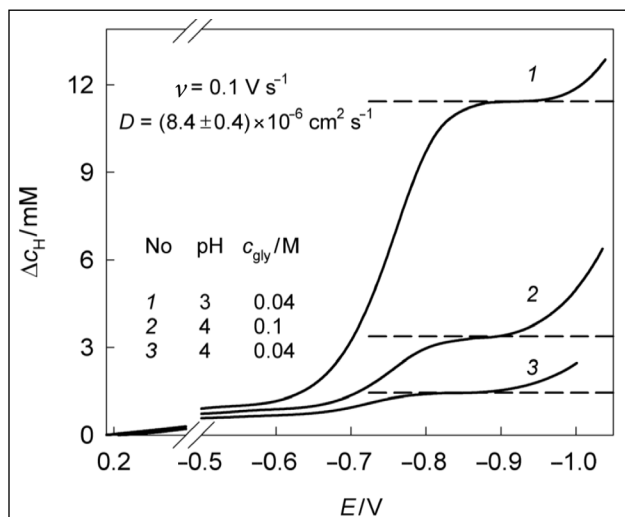

Fig. 5. Selected examples of voltammetric data transformed according to Eq. (5). Dotted lines show the respective bulk concentrations of labile proton donors determined by Eq (4)

CONCLUSIONS

1. LPS voltammetric data obtained for hydrogen evolution on the copper electrode in weakly acidic glycine solutions can serve as the basis for the estimation of electrochemical lability of different glycine species.

2. Current peaks and their potentials vary linearly with $\sqrt{v}$ and log v, respectively, this being typical of the electrochemical processes controlled by diffusion and charge transfer.

3. The dependence of current peaks on both solution pH and glycine concentration shows that some protonated glycine species can act as proton donors in hydrogen evolution.

4. The analysis of peak coordinates and convolutive transforms of voltammograms shows that protons attached to different groups in a glycine molecule exhibit different mobility. In contrast to the protonated amino group, the release of a proton from the carboxylic group proceeds significantly faster. Consequently, protonated $^+$H$_3$N–CH$_2$–COOH species can be treated as labile proton donors, whereas zwitterions $^+$H$_3$N–CH$_2$–COO$^-$ do not fall into this category.

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Arvydas Survila, Stasė Kanapeckaitė

GLICINO ELEKTROCHEMINIS LABILUMAS RŪGŠČIOSE TERPĖSE

S a n t r a u k a

Remiantis vandenilio skyrimosi silpnai rūgščiuose glicino tirpaluose voltamperiniais duomenimis, gautais skleidžiant potencialą įvairiais greičiais (v), nagrinėjamas įvairių glicino atmainų elektrocheminis labilumas. Voltamperogramos turi gerai išreikštas srovių smailes, kurių aukštis priklauso ir nuo pH, ir nuo glicino koncentracijos. Smailių srovių ir potencialų priklausomybės nuo $\sqrt{v}$ ir log v yra tiesinės (atitinkamai). Tai būdinga elektrocheminiams procesams, kuriuos kontroliuoja difuzija ir krūvio pernaša.

Sistemos labilumui charakterizuoti analizuojamos smailių koordinatės ir konvoliucinės voltamperogramų transformacijos. Rezultatai parodo, kad protonai, prijungti prie skirtingų glicino grupių, rodo skirtingą mobilumą. Kitaip negu protonuotos amino grupės atveju, protono atskilimas nuo karboksilinės grupės vyksta gerokai greičiau. Taigi protonuotą $^+$H$_3$N–CH$_2$–COOH atmainą galima priskirti labiliems protonų donorams, o cviterjonas $^+$H$_3$N–CH$_2$–COO$^-$ į šią kategoriją nepatenka.